

## THE STRUCTURE OF ATHABASCA ASPHALTENES AND THE CONVERSION OF THESE MATERIALS TO USEFUL BY-PRODUCTS

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### INTRODUCTION

The last decade has seen phenomenal development of gas-chromatographic and spectroscopic techniques which has enhanced identification of the constituents of lower boiling fractions of crude oils. However, the heavy ends of petroleum, i.e., the asphaltenes, have not been so readily identified but by application of chemical and physical methods to the problem of asphaltene structure, a number of significant details have been gathered from which it has been possible to propose a general model of asphaltene structure. One of these methods, proton magnetic resonance (p.m.r.) spectroscopy, has recently been evaluated (1,2,3,4) as a tool in the structural analysis of fractions of petroleum oils and asphalts and the results indicated (5) that petroleum asphaltenes are basically peri-condensed aromatic ring systems, having six to twenty aromatic nuclei, bearing alkyl and naphthenic moieties, with the hetero-atoms liberally scattered throughout in a variety of locations, including heterocyclic systems.

Subsequent application of the p.m.r. method to fractions of Athabasca bitumen (6) allowed the average chemical structures of the constituents to be expressed in terms of carbon-type distribution. Moreover, it was also possible to estimate the average structures of the aromatics within the fractions of the bitumen by relating the ratios of peripheral aromatic carbons to total aromatic carbons to those of known fused ring compounds. In general terms, an average asphaltene molecule appeared to consist of four or more aromatic sheets, containing ten or more rings each. Each condensed aromatic ring system carried individual alkyl side chains (four or five carbon atom units), which may or may not be linked to other aromatic sheets, together with smaller proportions of naphthenic rings which were presumably fused to the aromatic ring system.

The desirability of removing the asphaltene fraction from a crude oil has been advocated many times, the principal reasons being the production of a cracking stock low in metal impurities, hetero-atom (i.e. nitrogen, oxygen, and sulphur) compounds, and having a low carbon residue (7). The present paper is the outcome of a more detailed structural analysis of the Athabasca asphaltenes describing the average structures of the constituents within sub-fractions of the asphaltenes, with passing reference to the structures of the asphaltenes from forty-five conventional Alberta crudes, and, in conjunction with the chemical evidence provided herein, affords an indication of the potential of these heavy ends of crude oils.

## EXPERIMENTAL

Materials and General Techniques

Asphaltenes from Athabasca bitumen and from forty-five conventional Alberta crude oils were obtained by a standardized procedure described elsewhere (6). Fractionation of the Athabasca asphaltenes was achieved by treatment of the washed and dried asphaltenes with a series of higher molecular weight paraffinic solvents whereby, a soluble fraction (e.g. A<sub>1</sub>) and an insoluble fraction (e.g. B<sub>1</sub>) were obtained as shown below.

Fractionation of Athabasca Asphaltenes

	----- Fractions -----							
	A <sub>1</sub>	B <sub>1</sub>	A <sub>2</sub>	B <sub>2</sub>	A <sub>3</sub>	B <sub>3</sub>	A <sub>4</sub>	B <sub>4</sub>
% bitumen	1.0	16.0	1.8	15.2	3.4	13.6	6.0	11.0
% asphaltenes	5.9	94.1	10.6	89.4	20.0	80.0	35.3	64.7

Physical and Elemental Analyses

Elemental compositions of the fractions were determined by the Alfred Bernhardt Micro-analytical Laboratory, Elbach uber Engelskirchen, West Germany; the oxygen content of the samples was determined directly and not by difference. Molecular weights were measured osmotically. P.m.r. spectra were obtained in duplicate with a Hitachi Perkin-Elmer R20 High Resolution NMR Spectrometer using tetramethylsilane as internal standard as described previously (6). Furthermore, by means of the same principles as outlined previously (6) certain structural parameters were estimated which, with the exception of (e), are independent of the observed molecular weight, and are:

- (a)  $C_{SA}/C_p$ , the ratio of carbon atoms directly attached to an aromatic sheet to peripheral carbon atoms;  $C_{SA}/C_p$  is the average degree of substitution of the aromatic sheet.
- (b)  $C_S/C_{SA}$ , the ratio of saturated carbon atoms to carbon atoms attached to the edge of the aromatic sheet; the  $C_S/C_{SA}$  ratio indicates the average number of carbon atoms attached to a position on the edge of an aromatic sheet.
- (c)  $C_p/C_A$ , the ratio of peripheral carbon atoms per aromatic sheet to aromatic carbon atoms, i.e., an estimate of the average shape of the aromatic sheets.
- (d)  $(C_S - C_{Me})/C_{Me}$ , the ratio of methylene carbon to methyl carbon, i.e., an estimate of the degree of branching in the saturated moieties of the molecules.
- (e)  $R_A$ , the number of aromatic rings per molecule.

The results are illustrated in Table I and the  $C_p/C_A$  ratios for a series of standard condensed aromatics are presented in Table II in order to illustrate more clearly the closest possible ring structures of the aromatics.

## RESULTS

Structures in Asphaltene Fractions

The structural parameters presented in Table I offer information about the average struc-

TABLE I Structural Parameters of the Constituents  
in the Athabasca Asphaltene Fractions

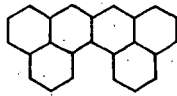
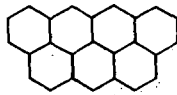
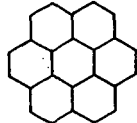
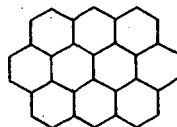
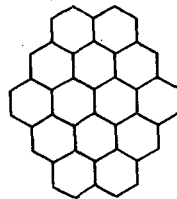
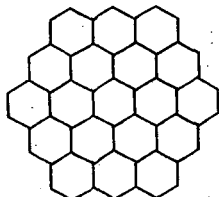
Sample	Molecular weight	-----Structural Parameters-----				Aromatic rings $R_A$
		$C_{SA}/C_P$	$C_S/C_{SA}$	$C_P/C_A$	$(C_S-C_{Me})/C_{Me}$	
A <sub>1</sub>	2,694	0.57	3.6	0.55	8.2	20.6
A <sub>2</sub>	2,704	0.62	3.5	0.54	8.2	20.7
A <sub>3</sub>	3,185	0.57	4.1	0.48	9.4	27.6
A <sub>4</sub>	4,338	0.65	3.1	0.46	4.4	40.8
B <sub>1</sub>	6,427	0.49	5.8	0.37	4.4	66.3
B <sub>2</sub>	6,530	0.48	6.0	0.37	4.6	67.8
B <sub>3</sub>	7,603	0.49	5.7	0.35	4.5	82.1
B <sub>4</sub>	8,158	0.52	5.0	0.35	4.6	90.3

tures of the Athabasca asphaltene fractions. For example, comparison of the  $C_P/C_A$  ratios with those of standard condensed aromatic compounds shows that the average structures of the asphaltenes vary from a dibenzonaphthacene, i.e., a six-ring unit in the lower molecular weight fractions to a least dinaphtho-ovalene, i.e., a fourteen-ring unit, in the higher molecular weight fractions. In keeping with this postulate of condensed aromatic structures, the asphaltenes form  $\pi$ -complexes with picric acid and with 1,3,5-trinitrobenzene which can be examined spectroscopically. Complexes of this type have been shown to be formed between condensed aromatics (e.g. pyrene, ovalene, etc.) and electron deficient nitro-aromatics (8).

From the  $C_{SA}/C_P$  parameters, 57-65% of the peripheral carbon atoms in the lower molecular weight asphaltenes (the A series) and 48-52% of the peripheral carbon atoms in the higher molecular weight fractions (the B series) carry saturated substituents. Moreover, the  $C_S/C_{SA}$  parameters show that these saturated substituents vary from a three to four carbon atom chain in the lower molecular weight fractions to a five to six carbon atom chain in the higher molecular weight fractions. In addition, the higher  $(C_S-C_{Me})/C_{Me}$  parameters of the lower molecular weight asphaltenes suggest a lower degree of branching in the saturated moieties. It would appear that the aromatic portions of the lower molecular weight asphaltenes carry unbranched alkyl substituents and unsubstituted naphthenic moieties whereas the aromatic sheets of the higher molecular weight asphaltenes bear branched alkyl and alkyl-substituted naphthenic moieties.

From p.m.r. and molecular weight data, each individual asphaltene molecule contains more than one aromatic sheet. For example, in the lower molecular weight asphaltenes where the  $C_P/C_A$  parameters indicate a six-, seven- or ten-ring basic unit, molecular weights indicate twenty to forty aromatic rings per molecule ( $R_A$ , Table I) which requires three or more basic units per asphaltene molecule. Similarly, in the higher molecular weight fractions where the basic unit is at least a fourteen-ring system, molecular weight data indicate that four to seven of these units constitute an asphaltene molecule. However, data obtained by the determination of molecular weights of the asphaltene fractions in solvents having different dielectric constants and in benzene at various temperatures suggest that the high molecular weights of the asphaltene molecules are due, in part, to electrostatic association of the individual units. These data, presented in Tables III and IV, show that a decrease in the observed molecular weight occurs when a solvent of higher dielectric constant or higher temperature is employed for the determination which suggests breakdown of  $\pi$ -electron interactions between individual asphaltene units under these conditions. A similar concept has been invoked to explain the high molecular weights of other crude oil asphaltenes (9) and the association of asphaltene units in dilute solution has also been reported (10).

TABLE II  $C_p/C_A$  Ratios of Condensed Aromatic Compounds

-----Hydrocarbon-----		
<u>Name</u>	<u>Structure</u>	<u><math>C_p/C_A</math></u>
Dibenzo[de,hi]naphthacene		0.58
Anthro[defghi]naphthacene		0.52
Coronene		0.50
Ovalene		0.44
Dinaphtho[2,7-hijk-2,7-stuv]-ovalene (Circopyrene)		0.38
Circocoronene		0.33

The present results also afford an indication of the limiting size of the individual sheets in the asphaltene molecules. A comparison of  $C_p/C_A$  ratios with the molecular weight (Table V) and a plot of these values shows that the limiting value for  $C_p/C_A$  is approximately 0.35, i.e., close to the  $C_p/C_A$  ratio of a fourteen-ring unit. Thus, it appears that any higher molecular weight fraction of the asphaltenes will be due to agglomerations of like, in this case dinaphtho-ovalene, nuclei and are probably approaching homogeneity. Larger units may approximate a coke-like structure.

Similar observations were recorded for asphaltenes from the forty-five conventional Alberta crudes; viz. the ring systems varied from six to fourteen aromatic nuclei per sheet with a tendency to associate in solution but there appeared to be higher proportions of naphthenic and

TABLE III Molecular Weight Determinations of Asphaltene Fractions in Different Solvents

<u>Sample</u>	<u>Solvent</u>	<u>Dielectric Constant*</u>	<u>Observed Molecular Weight</u>
A <sub>1</sub>	benzene	2.3	2,694
A <sub>1</sub>	methylene dibromide	7.8	2,239
A <sub>1</sub>	pyridine	12.3	1,382
B <sub>1</sub>	benzene	2.3	6,427
B <sub>1</sub>	methylene dibromide	7.8	4,804
B <sub>1</sub>	pyridine	12.3	3,413

\* Handbook of Chemistry and Physics, Chemical Rubber Co.

TABLE IV Relationship of Asphaltene Molecular Weight to Temperature of Solvent\*

<u>Temp. (°C)</u>	<u>Observed Molecular Weight**</u>
35	6,427
40	5,780
45	5,570
50	5,290
55	4,710

\* Solvent: benzene; sample: B<sub>1</sub>

\*\* Average of three determinations; the result of each determination was within  $\pm 3\%$  of the mean.

TABLE V Relationship of Asphaltene Cp/C<sub>A</sub> Ratios to Molecular Weights

<u>Fraction</u>	<u>Molecular Weight</u>	<u>C<sub>p</sub>/C<sub>A</sub></u>
A <sub>1</sub>	2,694	0.55
A <sub>2</sub>	2,704	0.54
A <sub>3</sub>	3,185	0.48
A <sub>4</sub>	4,338	0.46
B <sub>1</sub>	6,427	0.37
B <sub>2</sub>	6,530	0.37
B <sub>3</sub>	7,603	0.35
B <sub>4</sub>	8,158	0.35

alkyl moieties in these asphaltenes. It was also evident that the asphaltene structure was related to the age and nature of the sediment in which the oil was located but there did not appear to be any strict relationship between asphaltene content (% w/w) and viscosity (or "heaviness") of the crude oil. These results will be discussed in detail in a forthcoming publication.

## DISCUSSION

### Chemical Modification of Athabasca Asphaltenes

It is evident from the data assembled here that Athabasca asphaltenes are not entirely homogeneous and consist of large molecules and significantly smaller ones, i.e., the six-ring species, which are probably in the asphaltene fraction because of their high polarity, presumably due to their hetero-atom content, and hence their ability to associate in organic solvents. Nevertheless, as well as the conventional conversion of the asphaltenes to good grade coke, there are several other possible uses of the asphaltenes which can be brought about by carrying out simple chemical conversions of these carbonaceous materials. The progress of these reactions can be followed spectroscopically and the observations, which will be published in detail at a later date, are in agreement with a condensed aromatic ring-system bearing alkyl and naphthene substituents.

Oxidation with nitric acid, or other common oxidising agents, renders the asphaltenes water-dispersible and soluble in aqueous alkali which, when followed by sulphonation or sulphomethylation, yields water-soluble products (11). Halogenation with elemental halogen produces halo-derivatives of the asphaltenes (12) which, when fused with alkali, afford alkali-soluble materials. Introduction of the halogen as *p*-halophenyl via the Gomberg reaction (13) also affords a means of indirectly introducing functional groups or even introduction of the functional group in this manner affords useful products. Other useful reactions include carboxylation of the halo-asphaltenes via lithium/carbon dioxide; oxidation with *m*-dinitrobenzene and subsequent preparation of the imines; low temperature carbonization of the halo-asphaltenes via a Wurtz-Fittig or Ullmann reaction; conversion of the halo-asphaltenes to hydroxy-asphaltenes by caustic fusion; treatment with maleic anhydride and alkaline hydrolysis of the product affords a water-dispersible material which when treated with ammonia affords an acid dispersible product.

The overall effect of these and many other simple chemical reactions is to produce derivatives of the asphaltenes which may be gainfully employed. For example the incorporation of nitrogen or phosphorus into the molecule via the Gomberg reaction affords potentially useful slow-release fertilisers and soil conditioners as does the reaction of the carbonyl-asphaltenes with hydroxylamine or amines. Water-dispersible derivatives are useful as drilling mud thinners and soil conditioners whilst hydroxyl-containing derivatives can be used as ion-exchange resins or heat transfer media. Halo-asphaltenes are adequately suited for this latter purpose.

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